

Maximum Valency Lattice Gas Models

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Abstract

We study lattice gas models with the imposition of a constraint on the maximum number of bonds (nearest neighbor interactions) that particles can participate in. The critical parameters, as well as the coexistence region are studied using the mean field approximation and the Bethe-Peierls approximation. We find that the reduction of the number of interactions suppresses the temperature-density region where the liquid and gas phases coexist. We confirm these results from simulations using the histogram reweighting method employing grand Canonical Monte Carlo simulations.

I. INTRODUCTION

The study of the gel state of matter in colloidal systems is receiving significant attention in the last years[1, 2, 3, 4]. At the heart of this interest lies the hope that these studies will help understanding differences and similarities in the processes of formation of arrested states of matter at low packing fraction ϕ , and in particular the inter-relations between gels and glasses. A similarly ambitious additional goal is to provide a new route for understanding the intrinsic properties of the process of formation of physical gels in systems more complicated than colloids, as the case of gels formed by reversible cross-linking of polymeric chains[5] and gelation in protein solutions[6]. The full comprehension of both these aggregation processes are of extreme importance in the food industry, in the protein crystallization process and in the design of novel biomaterials[7].

One of the key questions regards the interplay between the process of formation of a long-living network and the process of phase separation in colloid-rich and colloid-poor regions[8, 9, 10, 11, 12]. Indeed, the increase of the bond interaction strength (relative to the thermal energy) controls both the increase of the inter-particle bond lifetime (and as a consequence the lifetime of the spanning network) and the increase of the driving force of formation of locally dense packed states, which progressively favor nucleation of the “liquid” (colloid-rich) phase[4]. As a result, the establishment of conditions such that a connected percolating structure able to sustain stress survives for times longer than the observation time is often preempted by phase separation. For spherical attractive interaction potentials, it has been found that phase separation is always dominant at low densities and arrested states at low packing fractions ϕ can be reached only in non-homogeneous state, whose morphology is determined by the phase separation process[13, 14, 15, 16, 17, 18, 19].

A possible mechanism to generate low packing fraction arrested states in the absence of phase separation has been recently proposed and supported by off-lattice simulations[20, 21]. It has been shown that the region in the $T - \phi$ plane in which a two-phase coexistence is thermodynamically preferred as compared to the homogeneous fluid state can be progressively reduced (both in T and ϕ) by decreasing the maximum number of possible pair-wise bonded interactions. In an equivalent language, the reduction — at fixed interaction potential range — of the colloid surface allowing for inter-particle bonding progressively destabilize phase separation[22, 23]. According to these ideas, colloidal particles with a limited number

of attractive spots are the best candidates for gel formation. Interestingly enough, these ideas carry also to the case of protein solutions, where the character of the amino acids on the surface of the protein controls the strength and the directionality of the inter-protein interaction[6].

In this article, we present a lattice gas model, which we solve in the Bragg-Williams mean field approximation and in the Bethe-Peierls quasi-chemical approximation and which allow us to visualize in a clear way the relation between the limitation of the maximum number of interaction and the amplitude of the phase separated region in the T - ϕ phase diagram. We complement these calculations with Monte Carlo simulations of the liquid-gas phase coexistence, to assess the reliability of the mean field solutions. The reported results confirm that the reduction of the maximum number of interactions is indeed an efficient mechanism for generating thermodynamically stable states at extremely low temperatures.

II. THE MODEL

The system we consider is a nearest neighbor lattice gas, with occupancy variables n_i at each node of a lattice with γ nearest neighbors.

The Hamiltonian for the system is written, in the usual form, as

$$H = -\epsilon \sum_{\langle ij \rangle}^* n_i n_j \quad (1)$$

but with the $*$ indicating that the sum is only over such bond configurations that have at each vertex a maximum of γ_m bonds.

For the purposes of mean field theory, we can write this as

$$H = -\frac{\epsilon}{2} \sum_i n_i f\left(\sum_j^{\gamma} n_j\right) \quad (2)$$

where the first sum i runs over all lattice sites, and the second sum j runs over all γ nearest neighbors of site i , and with

$$f(x) = x, \quad x \leq \gamma_m \quad (3)$$

$$= \gamma_m, \quad x > \gamma_m \quad (4)$$

where γ_m denotes the maximum number of interactions, or valency, allowed for a particle at any site. When $\gamma_m = \gamma$, one recovers the simple lattice gas. In the following, we consider

the behavior of the system when the parameter γ_m is varied between the limits $\gamma_m = 0$ (when one has a non-interacting *paramagnetic* lattice gas) and $\gamma_m = \gamma$ (when one has the simple nearest neighbor lattice gas).

III. MEAN FIELD APPROXIMATION

In order to perform the mean field calculation, we approximate the function f as

$$f(x) = \gamma_m \tanh(x/\gamma_m) \quad (5)$$

which has the desired linear behavior for small x and a constant value of γ_m at large x . Further, the mean field approximation amounts to writing $\sum_j^{nn} n_j = \gamma \langle n \rangle$ where $\langle n \rangle$ is the average occupancy, given by $\langle n \rangle = \sum_i n_i / N$ where N is the total number of sites. With this approximation, the thermodynamic potential Ω in the grand canonical ensemble may be written as

$$\Omega/N = -\frac{\epsilon}{2}\gamma_m \langle n \rangle \tanh\left(\frac{\gamma \langle n \rangle}{\gamma_m}\right) - \mu \langle n \rangle + k_B T [\langle n \rangle \log \langle n \rangle + (1 - \langle n \rangle) \log(1 - \langle n \rangle)] \quad (6)$$

where μ is the chemical potential, T is the temperature, k_B is the Boltzmann's constant and $\langle n \rangle$ is the occupancy, given μ and T , that minimizes Ω . Imposing the minimization condition,

$$\frac{\partial \Omega}{\partial \langle n \rangle} = 0$$

allows one to eliminate μ and write the thermodynamic potential Ω in terms of T and $\langle n \rangle$. Further, since $\Omega = -PV = -PN$, (where P is the pressure, and the system volume for the lattice gas $V = N$ the number of sites) one obtains in this way the equation of state of the system:

$$P = -\frac{\epsilon}{2}\gamma \langle n \rangle^2 \operatorname{sech}^2\left(\frac{\gamma \langle n \rangle}{\gamma_m}\right) - k_B T \log(1 - \langle n \rangle) \quad (7)$$

The condition for the critical point is given by

$$\frac{\partial P}{\partial \langle n \rangle} = 0$$

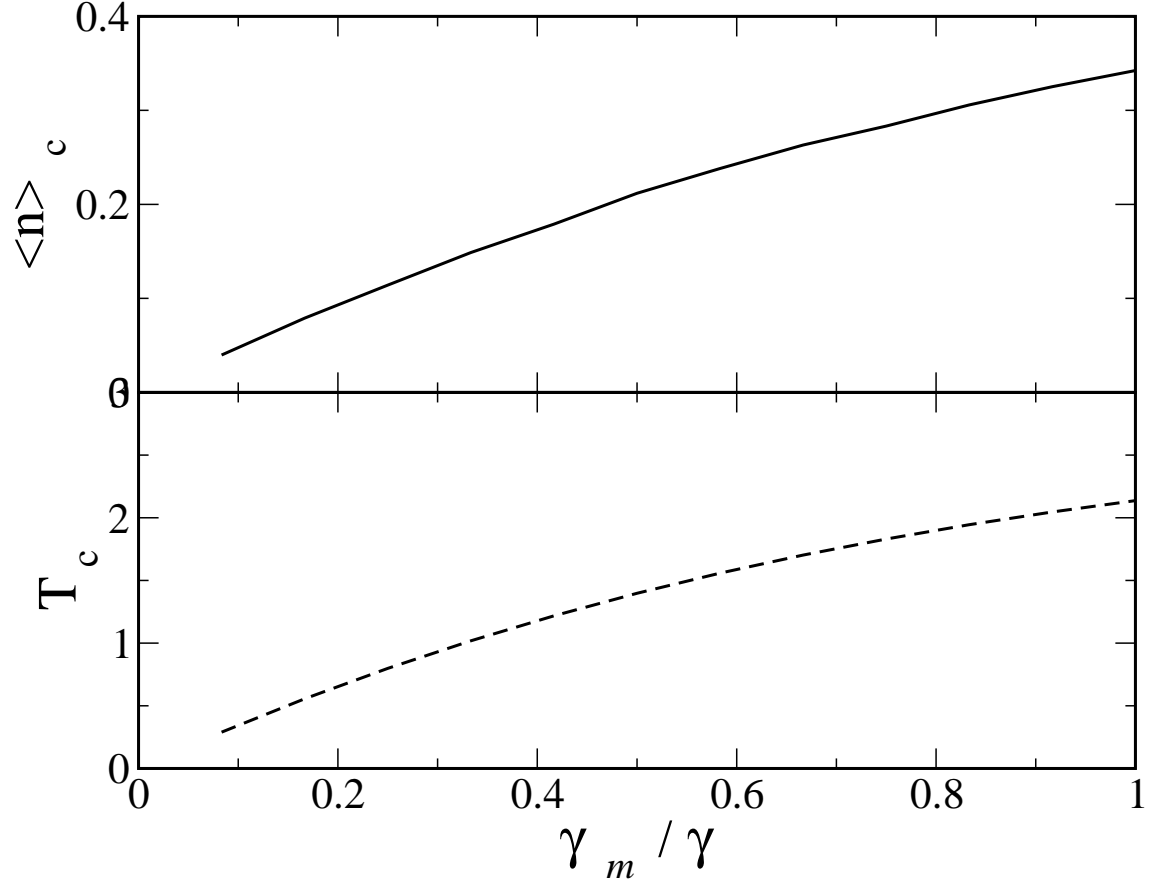


FIG. 1: Mean field critical density (top panel) and critical temperature (lower panel) as a function of parameter γ_m/γ . Calculated for $\gamma = 12$ and $\epsilon = 1$.

and

$$\frac{\partial^2 P}{\partial \langle n \rangle^2} = 0.$$

From these, one obtains the critical density and the critical temperature, which depend on the parameter γ_m/γ and are plotted in Fig. 1. From the figure, it is clear that both the critical density and the critical temperature go to zero as the variable γ_m/γ goes to zero.

We next calculate the spinodals that demarcate the region of instability in the $(\langle n \rangle, T)$ and in the $(\langle n \rangle, P)$ phase diagram which are shown in Fig. 2. Consistently with expectations based on the behavior of the critical density and temperature, the region of instability also shrinks with the reduction in the valency.

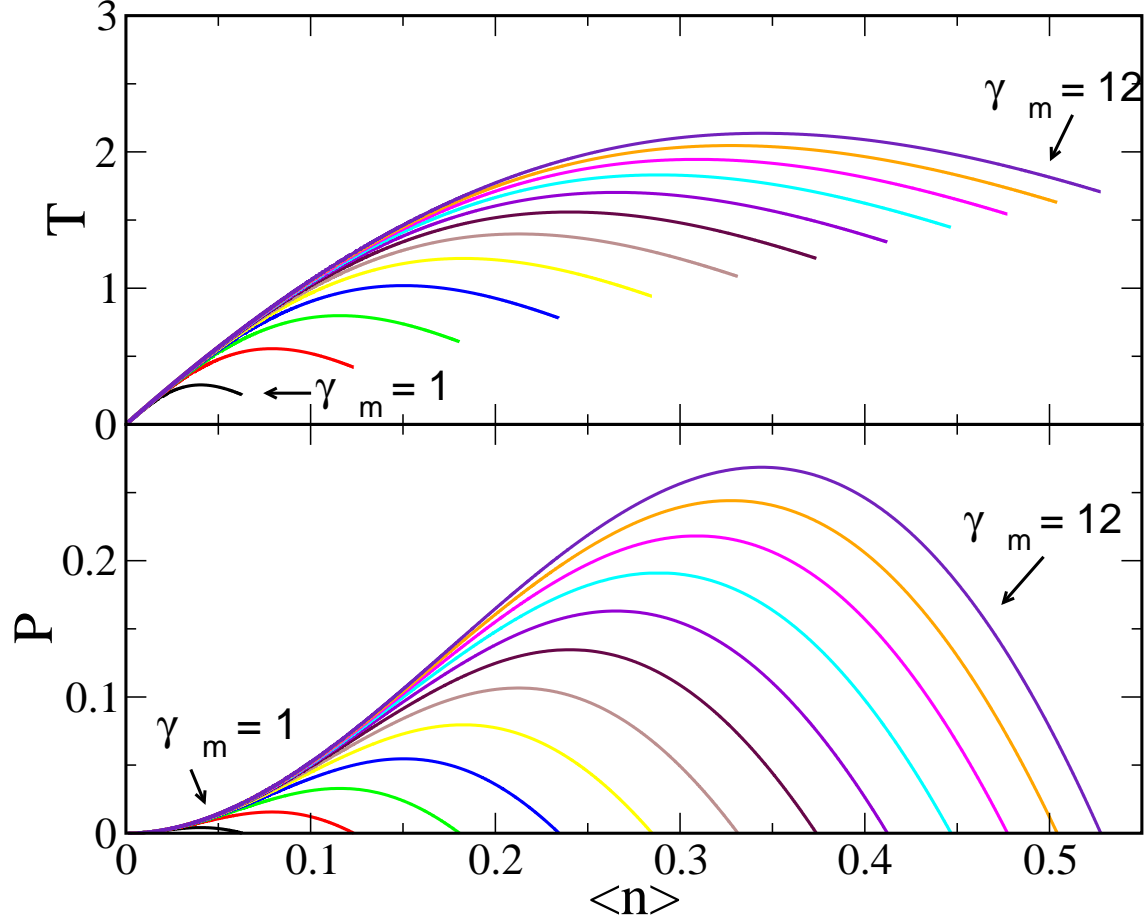


FIG. 2: The mean-field spinodals in the $(\langle n \rangle, T)$ phase diagram (top panel) and in the $(\langle n \rangle, P)$ phase diagram (lower panel) for different values of the parameter γ_m . Calculated for $\gamma = 12$ and $\epsilon = 1$.

IV. BETHE-PEIERLS APPROXIMATION

As an improvement over the mean field approximation, we next consider the Bethe-Peierls approximation, which in the case of the simple lattice gas is equivalent to the Bethe lattice. As in the standard treatment (see, *e. g.* [24]), we consider a “center” site, and its surrounding neighbors. We write the probability that the center site is occupied, with n nearest neighbors also being occupied, as

$$P(1, n) = \frac{1}{q} \exp(\beta\mu) C_n^\gamma \exp(\beta\epsilon n) \exp(\beta\mu n) z^n \quad n \leq \gamma_m \quad (8)$$

$$= \frac{1}{q} C_n^\gamma \exp(\beta\epsilon\gamma_m) \exp(\beta\mu n) z^n \quad n > \gamma_m \quad (9)$$

where $\beta \equiv 1/k_B T$, q is the normalization, and z is introduced to account for the influence of the rest of the lattice. The rest of the terms explicitly account for the interactions and the chemical potential corresponding to the number of occupied sites present. Similarly, the probability that the center site is not occupied, with n neighbors occupied, is

$$P(0, n) = \frac{1}{q} C_n^\gamma \exp(\beta \mu n) z^n \quad (10)$$

The normalization factor q is given by the condition

$$\sum_{n=0}^{\gamma} [P(1, n) + P(0, n)] = 1 \quad (11)$$

The average occupancy number $\langle n_0 \rangle$ for the the center site is the probability that the center is occupied regardless of the occupancy of the surrounding sites, that is:

$$\langle n_0 \rangle = \sum_{n=0}^{\gamma} P(1, n). \quad (12)$$

The average occupancy number $\langle n_e \rangle$ for a given neighbor site is given by

$$\langle n_e \rangle = \frac{1}{\gamma} \sum_{n=0}^{\gamma} n [P(1, n) + P(0, n)]. \quad (13)$$

The unknown parameter z is now determined by the condition that these two occupancy number, $\langle n_0 \rangle$ and $\langle n_e \rangle$ are both equal to $\langle n \rangle$. Defining a function

$$g(z, \mu, T) = \langle n_0 \rangle - \langle n_e \rangle,$$

the solution is found by the condition $g(z, \mu, T) = 0$. Determining z in this way, and using the expression for $\langle n_0 \rangle$ above, one obtains the probability of occupation as a function of T and μ . In addition, imposing the condition that the first and second derivatives of g also vanish yields the condition for the critical point, since this vanishing of the first and second derivatives marks the change from the high temperature regime where only one solution exists, to the presence of more than one solution at lower temperatures. In addition, the condition that the first derivative vanishes is used to locate the spinodal points. Figure 3 shows the dependence of the critical density, temperature, and the chemical potential on the parameter γ_m which is varied in integer steps for $\gamma = 12$. The case of $\gamma_m = \gamma$ reproduces the standard result for this approximation. It is seen that the critical temperature decreases

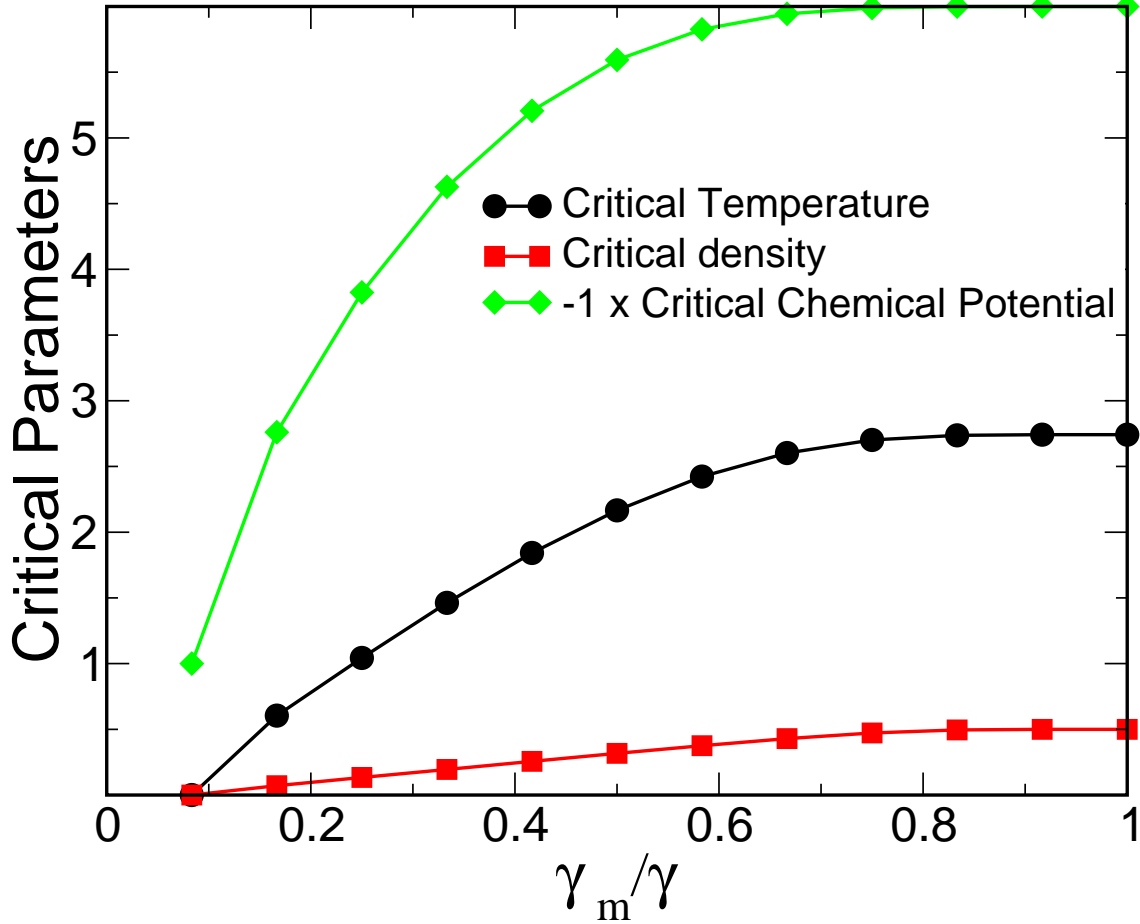


FIG. 3: Critical density and critical temperature as a function of parameter γ_m for the Bethe-Peierls approximation.

very slowly at first as γ_m is reduced, but goes to zero for $\gamma_m = 1$. Interestingly, the case of $\gamma_m = 2$ displays a finite critical temperature, which is somewhat surprising, since in this case the system can form only two bonds at each site, and one expects this to be equivalent to a one dimensional system with a vanishing critical temperature.

We next calculate the spinodals that demarcate the region of instability in the $(\langle n \rangle, T)$ phase diagram for $\gamma_m = 3$, which is shown in Fig. 4. As in the mean field case the region of instability also shrinks with the reduction in the valency.

V. SIMULATIONS

In order to estimate the accuracy of the approximations above, we evaluate the critical parameters and the co-existence lines for different values of γ_m using computer simulations,

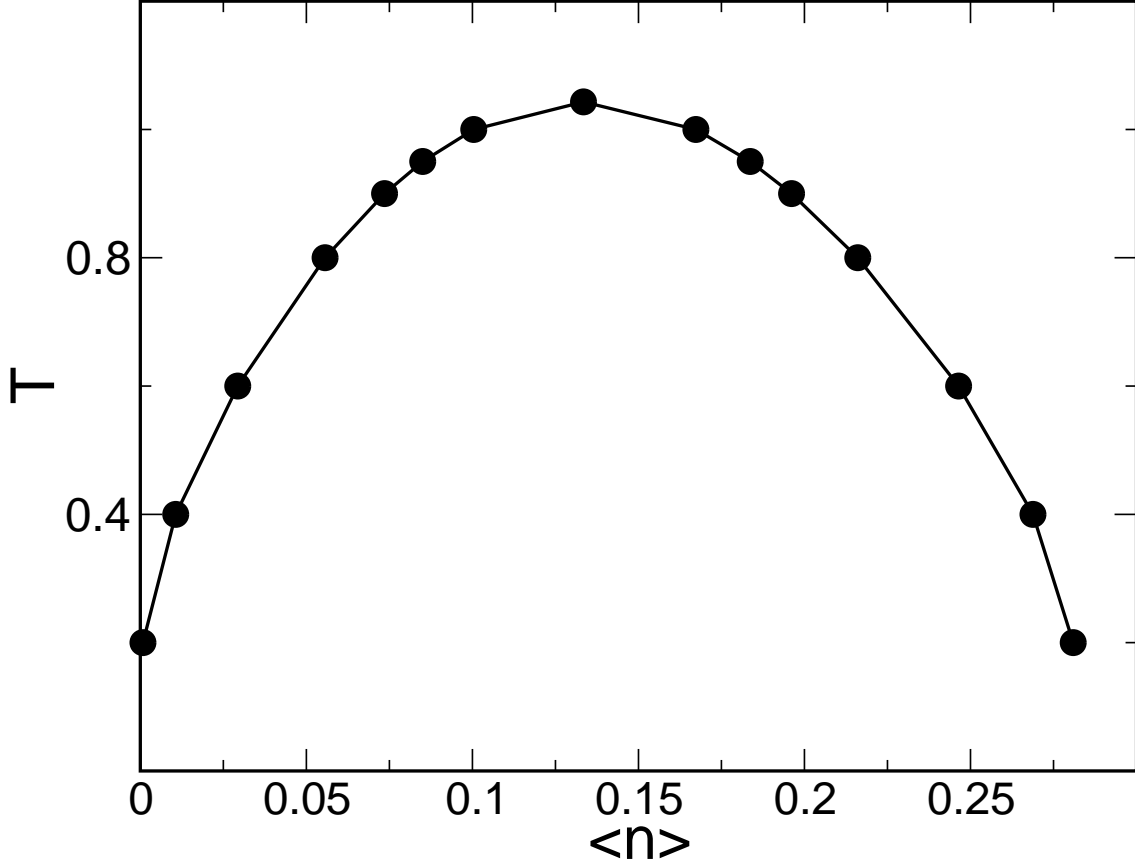


FIG. 4: The Bethe-Peierls spinodal line evaluated for the specific case of $\gamma = 12$ and $\gamma_m = 3$.

employing the histogram reweighting technique [25, 26, 27, 28]. In this method, histograms of sampled energies and number densities from simulations at different external parameters are used to estimate composite probability distributions, which in turn may be used to obtain information on phase equilibrium. To this end, we perform Monte Carlo simulations in the constant temperature and constant chemical potential ensemble for a lattice of 256 sites arranged in an *FCC* lattice. The energy of the system depends not only on which sites are occupied, but also which bonds exist in the system. Therefore, care must be taken that the formation and deletion of bonds obeys detailed balance. In the grand canonical simulations, it is sufficient, when a particle is inserted, to pick any of the possible bond configurations at random, with equal probability. At each simulated temperature and chemical potential, runs of length 2.5 million Monte Carlo cycles (MCS). The energies and number of particles every 100 MCS, after an equilibration of 0.5 million MCS, are used to build histograms $f_i(N, E)$ (where N is the number of particles and E is the energy), where $i = 1 \dots R$ indexes the different runs at different μ and T values. As described in [26, 28], the composite probability

distribution $\Gamma(N, E, \mu, \beta)$ is obtained with

$$\Gamma(N, E, \mu, \beta) = \frac{\sum_{i=1}^R f_i(N, E) \exp(-\beta E + \beta \mu N)}{\sum_{i=1}^R K_i \exp(-\beta_i E + \beta_i \mu_i N - C_i)} \quad (14)$$

where K_i is the total number of observations for each run, and the constants C_i are obtained iteratively from the relationship

$$\exp(C_i) = \sum_E \sum_N \Gamma(N, E, \mu_i, \beta_i). \quad (15)$$

Once the above equations are run to convergence, the probability distribution in particle number can be obtained by summing Γ over the energies. Phase co-existence at any given temperature is obtained by requiring that the distribution with respect to density has two distinct peaks, of equal height. Figure 5 shows the coexistence curves obtained for the cases $\gamma_m = 12, 9, 6$. Studying phase coexistence at lower values of γ_m is severely hampered by the extremely slow equilibration in the temperature range of interest and has not been attempted. In each of the cases studied, evaluating the coexisting phase densities is limited by the ability resolve the coexisting density peaks, which is difficult as the critical point is approached. Nevertheless, it is clear from the data shown that the simulations confirm the trend seen in the calculations above, that the critical temperature, density and (minus) the chemical potential decrease as γ_m decreases. Figure 6 shows the critical parameters in comparison with the Bethe-Peierls calculations. It is seen that the critical parameters drop more rapidly than suggested by the Bethe-Peierls calculations. Unlike the $\gamma_m = 12$ case, where the coexistence chemical potential and the mean of the coexisting densities are constant below the critical temperature, both these quantities increase as one moves to lower temperatures below the critical temperature.

VI. CONCLUSIONS

We have presented results for lattice gas models with the imposition of a constraint on the maximum number of bonds that particles can participate in. Mean field (Bragg-Williams and Bethe-Peierls) calculations and computer simulations using the histogram reweighting technique, show that the critical temperature and density decrease as the maximum number of bonds allowed for a given particle is reduced. Also, we find that the density range of the

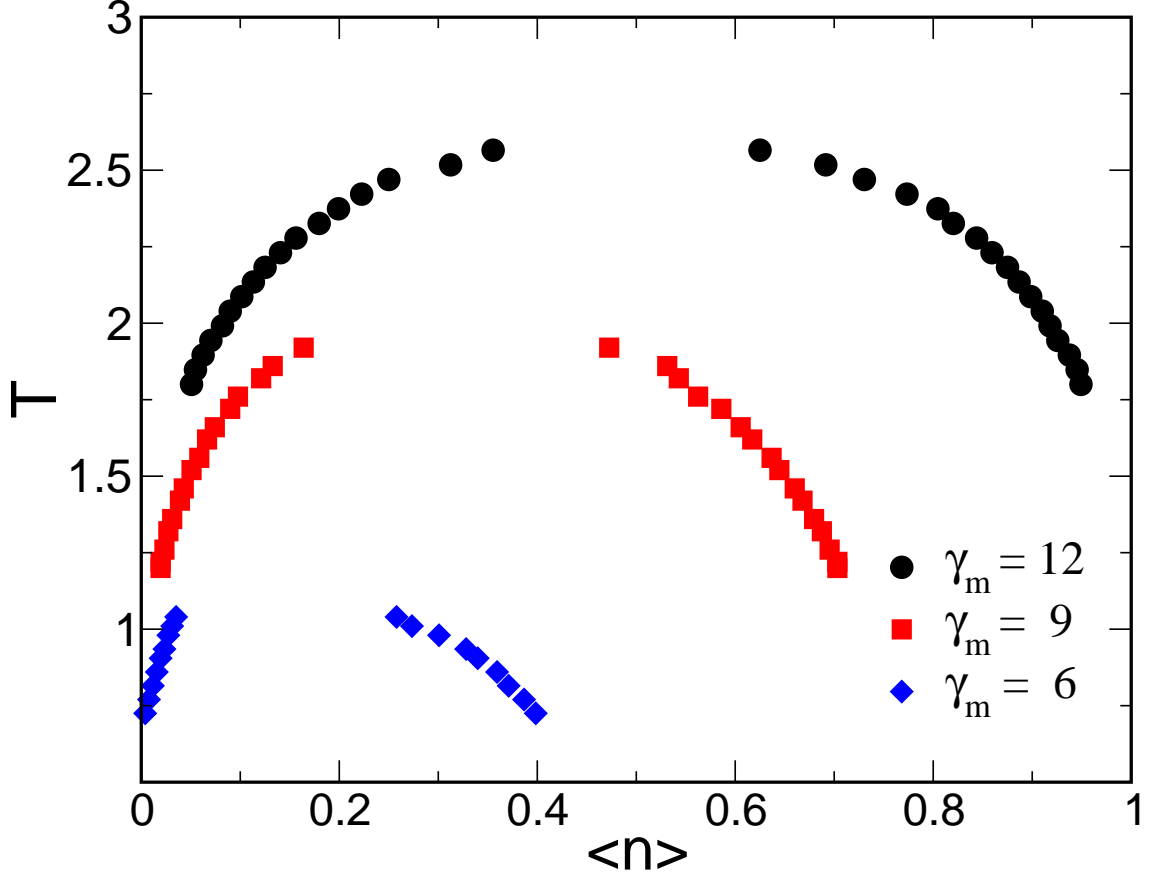


FIG. 5: The coexistence curves for $\gamma_m = 12, 9, 6$ from simulations, showing that the coexistence region shrinks as γ_m decreases.

coexistence region, where the liquid and gas phases coexist, shrinks as the maximum valency of the particles is reduced. These results are consistent with the results that have been obtained earlier for similarly defined continuum models [20, 21]. It is thus confirmed that valency reduction is effective in opening a large region of densities in which low temperature disordered states can be accessed in equilibrium. Studies of models with controlled valency, both on the lattice and off-lattice, may make it possible to disentangle gelation from phase separation.

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- [1] N. A. M. Verhaeg, D. Asnaghi, H. Lekkerkerker *Physica A* **264** (1999) 64.
 - [2] V. Trappe and P. Sandkühler, *Current Opinion in Colloid and Interface Science* **8** 494 (2004).
 - [3] L. Cipelletti and L. Ramos, *J. Phys.: Condens. Matter* **17** R253 (2004).

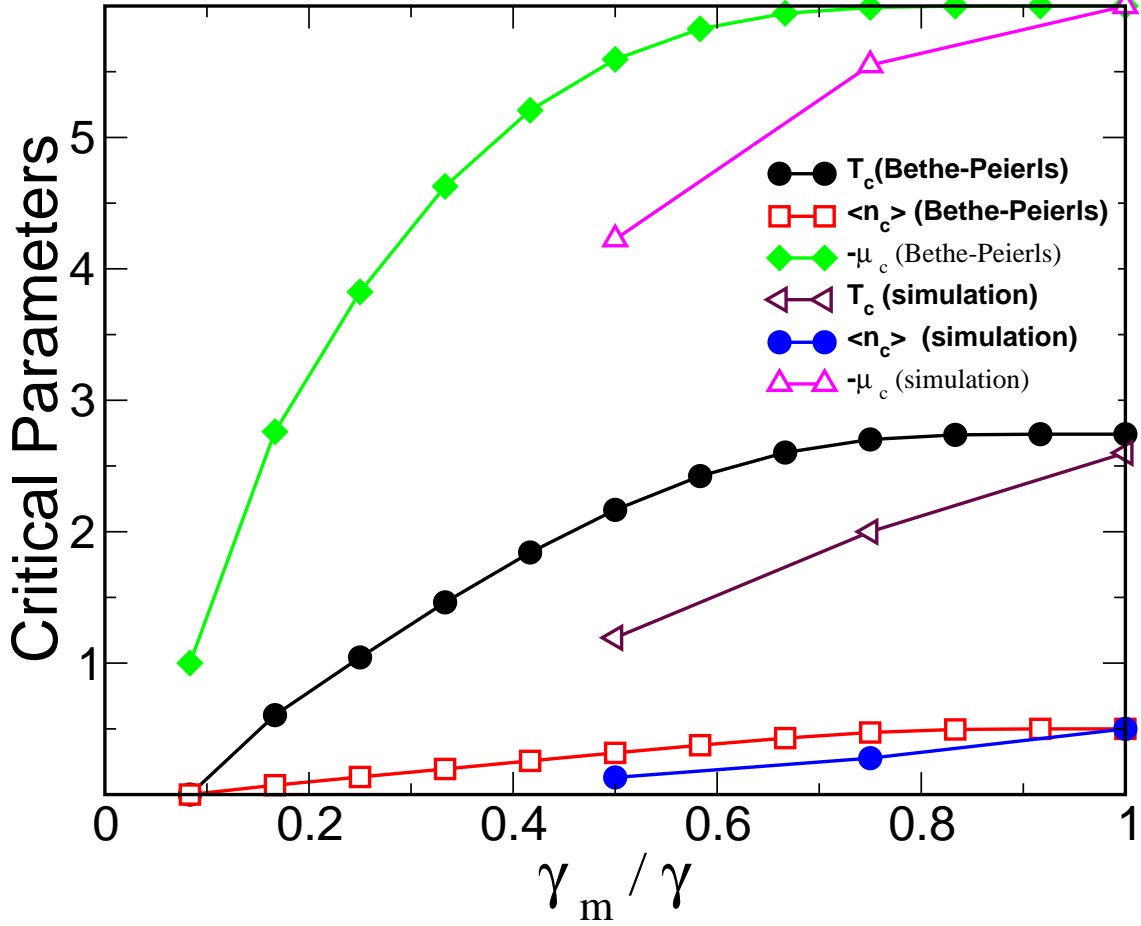


FIG. 6: Comparison of the critical parameters from simulation with those of the Bethe-Peierls approximation, indicating that the critical parameters decrease more rapidly than suggested by the Bethe-Peierls approximation.

- [4] F. Sciortino *et al.*, Comput. Phys. Comm. **169** 166 (2005).
- [5] M. Rubinstein and A.V. Dobrynin, Curr. Opin. Colloid Interface Sci. **4**, 83 (1999).
- [6] A. Lomakin, N. Asherie and G. B. Benedek, Proc. Natl. Acad. Sci., **96**, 9465 (1999).
- [7] F. W. Starr and F. Sciortino, *J. Phys: Condens. Matter* **18**, L347 (2006).
- [8] J. F. M. Lodge and D. M. Heyes, Phys. Chem. Chem. Phys. **1**, 2119 (1999).
- [9] J. Bergenholtz M. Fuchs, *Phys. Rev. E* **59**, 5706 (1999).
- [10] M. E. Cates *et al*, *J. Phys. Cond. Matter* **16**, S4861 (2004).
- [11] E. Del Gado, A. Fierro, L. de Arcangelis and A. Coniglio, *Phy. Rev. E.* **69**, 051103 (2004).
- [12] E. Zaccarelli, F. Sciortino, S. V. Buldyrev and P. Tartaglia, in *Unifying Concepts in Granular Media and Glasses*, edited by A. Coniglio, A. Fierro, H.J. Herrmann, M. Nicodemi (Elsevier,

Amsterdam, 2004), pp. 181.

- [13] S. Sastry, *Phys. Rev. Lett.* **85**, 590 (2000).
- [14] R. J. Speedy, *J. Phys. Cond. Matt* **15**, S1243 (2003).
- [15] E. La Nave, S. Mossa, F. Sciortino and P. Tartaglia, *J. Chem. Phys.* **120**, 6128 (2004).
- [16] M. S. Shell and P. G. Debenedetti, *Phys. Rev. E* **69**, 051102 (2004).
- [17] S. S. Ashwin, G. I. Menon and S. Sastry, *Europhys. Lett* **75**, 922 (2006).
- [18] G. Foffi, C. De Michele, F. Sciortino and P. Tartaglia, *J. Chem. Phys* **122**, 224903 (2005).
- [19] S. Manley *et al*, *Phys. Rev. Lett.* **95**, 23802 (2005).
- [20] E. Zaccarelli *et al*. *Phys. Rev. Lett.* **94**, 218301-1 (2005).
- [21] E. Bianchi *et al*, <http://www.arxiv.org/abs/cond-mat/0605701>.
- [22] R. P. Sear, *J. Chem. Phys.* **111**, (1999) 4800.
- [23] N. Kern, D. Frenkel, *J. Chem. Phys.* **118**, (2003) 9882.
- [24] K. Huang, *Statistical Mechanics* (John Wiley and Sons, New York, 2000).
- [25] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett* **61**, 2635 (1988).
- [26] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett* **63**, 1195 (1989).
- [27] A.Z. Panagiotopoulos, V. Wong and M.A. Floriano, *Macromolecules* **31** (**3**), 912 (1998).
- [28] A.Z. Panagiotopoulos, *J. Phys. Condens. Matter*, **12**, R25 (2000).